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A Nano-composite Carbon Paste Lanthanum(III) Sensor

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Based on our previous studies which indicated a strong interaction between 8-amino-N-(2-hydroxybenzylidene) naphthyl amine (ANA) with La(III) ions, ANA was used as a sensing material in a nano-composite based carbon paste electrode. The electrodes were made based on a nano-composite including multi-walled carbon nanotube (MWCNT), graphite, and room temperature ionic liquid (RTIL), 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4. The best results were obtained for the nano-composite sensor with electrode composition of 5% MWCNT, 10% ANA, 15% RTIL, and 70% graphite powder. The proposed sensor shows a Nernstian response (19.8±0.3 mV $decade^{-1}$) in the range of 1.0×10^{-6}-1.0×10^{-2} M with detection limit of 8.0×10^{-7} M. The response of the sensor is independent of pH in the range of 4.0-9.0. The nano-composite based La(III) sensor displayed good selectivity, response time, and lifetime.

Keywords: Sensor, ion selective electrode, potentiometry, carbon paste, multi-walled carbon nanotubes, ionic liquid

1. INTRODUCTION

Lanthanum oxide is used in making of optical glasses, manufacturing of glass fibers for optical purposes, and using as catalysts in gasoline-cracking. It is also used in polishing compounds, carbon arcs, and removing sulfur, carbon, and other electronegative elements from iron and steel in iron and steel industries [1]. Lanthanum chloride manifests as anti-tumor compound too [2].

There are a number of methods for low-level determination of La(III) ions in solutions, include spectrophotometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), isotope dilution mass spectrometry, neutron activation analysis, X-ray fluorescence spectrometry [3-7]. These methods have one or more of disadvantages including a) time consuming, b) multiple sample manipulations, and c) too expensive for most analytical laboratories.

Recently, potentiometric sensors are used as new method which offers an inexpensive and convenient method for monitoring of a number of cations and anions in solutions, within acceptable sensitivity and selectivity. In recent decade a number of potentiometric sensors for La(III) and other lanthanide ions have been reported by our team using different sensing materials mostly Schiff's bases and hydrazones [8-26].

One of the most important types of potentiometric sensors is carbon paste electrode. This is most probably due to the improved renewability, stable response, and low ohmic resistance of CPEs in comparison with other types of potentiometric sensors [27-35]. A typical potentiometric CPEs is based on a mixture of sensing material, graphite powder and a non-conductive mineral oil as binder, which is called carbon paste.

Recently, room temperature ionic liquids (RTIL) with a number of favorite properties such as good solvating properties, high conductivity, non-volatility, low toxicity, good electrochemical and chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity were used as binder in CPEs [35-39].

Addition of multiwall carbon nanotubes (MWCNTs) with special physicochemical properties such as ultra-light weights, high mechanical strengths, high electrical conductivities, high thermal conductivities, metallic or semi-metallic behaviors and high surface areas to CPEs, causes improvement of response of this type of sensor [40-43]. In this work a highly selective La(III) modified carbon paste sensor is introduced.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The cell used for the potential measurements of the nano-composite based La(III) sensor as the indicator electrode and an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode both of which were connected to a mili-voltmeter.

The cell assembly constructed for the conduction of electromotive force (Emf) measurements is as follows;

Nano-composite based sensor | sample solution | Ag/AgCl–KCl (satd.)

2.2. Reagents and materials

Graphite powder with a 1–2 μm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for construction of the carbon pastes. The ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and chloride and nitrate salts of the cations were purchased from Merck and used as received. The multi-walled carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length, SBET: 40-600 m^2/g and with 95% purity were purchased from Research Institute of the

Petroleum Industry (Tehran, Iran). The procedure for the preparation of 8-amino-N-(2-hydroxybenzylidene) naphthyl amine (ANA) has been previously reported [44].

2.3. Electrode Fabrication

The modified CPEs were prepared through a general procedure as follows: The desired amounts of the ionophore ANA along with an appropriate amount of graphite powder, ionic liquid or paraffin oil and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube of 5 mm i.d. and a height of 3 cm. The mixture was then homogenized before being packed into the tube tip to avoid possible air gaps which can increase the electric resistance of the electrodes. A copper wire was then inserted into the opposite end of the modified CPE to establish electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 72 h by soaking it in a 1.0×10^{-3} M $La(NO_3)_3$ solution [28-35].

3. RESULTS AND DISCUSSION

3.1. Optimization of CPEs

The sensing material or ion carrier used as the main ingredient of any ion-selective sensors is known to strongly influence the selectivity of such devices [45-50]. Based on our previous studies [44] which indicated a strong interaction between 8-amino-N-(2-hydroxybenzylidene) naphthyl amine (ANA) (Fig. 1) with La(III) ions, it was used in fabrication of a series of nano-composite CPEs with a variety of compositions some of which were modified using the ionic liquid and MWCNT. The compositions of these sensors are given in Table 1. As it can be seen, in the absence of the ionophore ANA (compositions 1-3) in the composition of the carbon paste electrode, the responses of the sensors are very weak. It was also observed that changing the amounts of the graphite powder as the filler and paraffin, does not significantly change the potential response of the sensor.

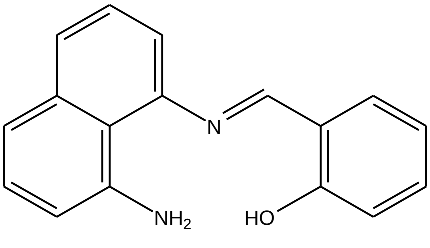

Figure 1. Chemical structure of ANA

The addition of ionophore ANA to the compositions increase in the potential responses of the CP electrodes (composition 4-7). As it is seen, addition of 10% ANA to CP electrode increases the slope of CP electrode from 4.4±0.2 to 14.9±0.3 mV decade^{-1}. Which is based on the previous observations, due to the enhanced and as was later observed, this was a further support to the initial assumptions made about the selective tendency of ANA towards La(III) ions. Further increase in the amount of the amount of the ionophore to 12% wt. (no. 7), however, did not lead to any considerable changes in the response of the electrode. It was hence decided that 10% wt. is the optimum amount of the ionophore in the CPE.

Table 1. The optimization of the nano-composite based La(III) carbon paste ingredients

No.	Composition (%)					Slope (mV decade^{-1})	Linear range (M)	R^2
	ANA	Graphite	Paraffin	RTIL	MWCNT			
1	--	90	10	-	--	4.1 ± 0.1	1.0×10^{-2} - 1.0×10^{-4}	0.895
2	--	85	15	-	--	4.4 ± 0.2	1.0×10^{-2} - 1.0×10^{-4}	0.873
3	--	80	20	-	--	4.3 ± 0.3	1.0×10^{-2} - 1.0×10^{-4}	0.888
4	5	80	15	-	-	11.2 ± 0.2	1.0×10^{-2} - 1.0×10^{-5}	0.908
5	7	78	15	-	--	13.9 ± 0.1	1.0×10^{-2} - 1.0×10^{-5}	0.987
6	10	75	15	-	--	14.9 ± 0.3	1.0×10^{-2} - 4.0×10^{-5}	0.993
7	12	73	15	-	--	14.8 ± 0.2	1.0×10^{-2} - 4.0×10^{-5}	0.993
8	10	73	15	-	2	17.7 ± 0.4	1.0×10^{-2} - 2.0×10^{-6}	0.986
9	10	70	15	-	5	18.2 ± 0.3	1.0×10^{-2} - 1.0×10^{-6}	0.991
10	10	68	15	-	7	18.2 ± 0.2	1.0×10^{-2} - 7.5×10^{-6}	0.997
11	10	70	-	15	5	19.8 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}	0.994

As can be seen from Table 1, unmodified CPEs having the optimized composition (electrode no. 6) shows a sub-Nernstian slope of ~14.9 mV decade^{-1} of La(III) activity. The electrode compositions were further modified by adding %2, %5 and %7 wt. of MWCNT to the composition (Nos. 8-10) which led to improvements in the potential response of the sensor from the value of 14.9±0.3 mV decade^{-1} to 18.2±0.2 mV decade^{-1}. This is due to improving the conductivity of the composition, which in turn changes the chemical signal to an electrical one.

As it is seen from the data in Table 1, replacing the paraffin oil (no. 9) with RTILs (no. 11) within better extraction capabilities in the CPE, increases the potential response slope about 1.6 mV decade^{-1} of concentration due to increasing the extraction of high charge-density La(III) cations therein, it is most probably due to the much higher dielectric constant of the latter.

However, as can be seen from Table 1 a composition of 10% ANA, 15% [bmim]BF_4, 70% graphite powder, 5% MWCNT was chosen as the optimum composition showing a Nernstian slope of 19.8±0.2 mV decade^{-1}.

3.2. Measuring range and detection limit

The response of the nano-composite based La(III) CPE (no. 11) was further tested in La(III) ion concentration range of 1.0×10^{-1}-1.0×10^{-8} M and the results are depicted in Fig. 2. As it is well known in the literature the measuring range of the CPE is defined as the activity range between its upper and lower detection limits [51-55]. The applicable range of the CPE with a composition according to no. 11 ranges from 1.0×10^{-2}-1.0×10^{-6} M (Fig. 2).

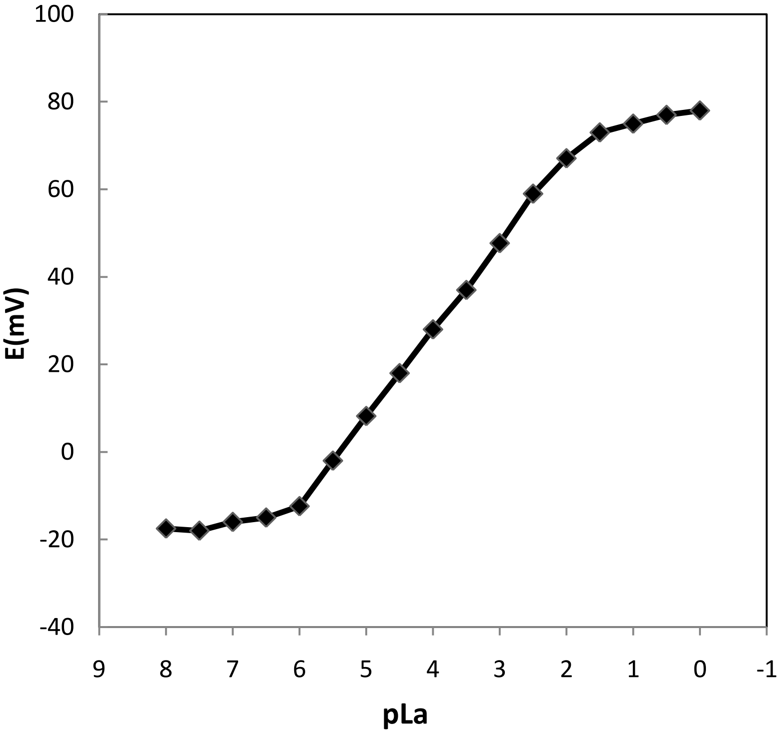

Figure 2. The calibration curve of the La(III) nano-composite CPE based on ANA (Electrode no. 10)

To calculate the detection limits of the CPE extrapolation of the linear portion of the electrode's calibration curve was used and this parameter found to be 8.0×10^{-7} M.

3.3. Effect of pH

pH effect on the potential response of the best nano-composite CPE (no. 10), was considered by recording of the potential shown by the sensor in a 1.0×10^{-4} M La(III) ion solution while varying the pH values. pH of the solution was varied from (1-12) by adding concentrated HNO_3 or NaOH solutions thereto. The recorded potentials as a function of pH are depicted in Fig. 3. As can be seen from Fig. 3, the response of the sensor is independent from pH in the range from 4.0-9.0. Potential fluctuations at pH values greater than 9.0 are due to the formation of some soluble or insoluble lanthanum hydroxy complexes. At lower pH values than 4.0 can be attributed to partial protonation of the donor atoms of ANA in the fabricated sensor [17-22].

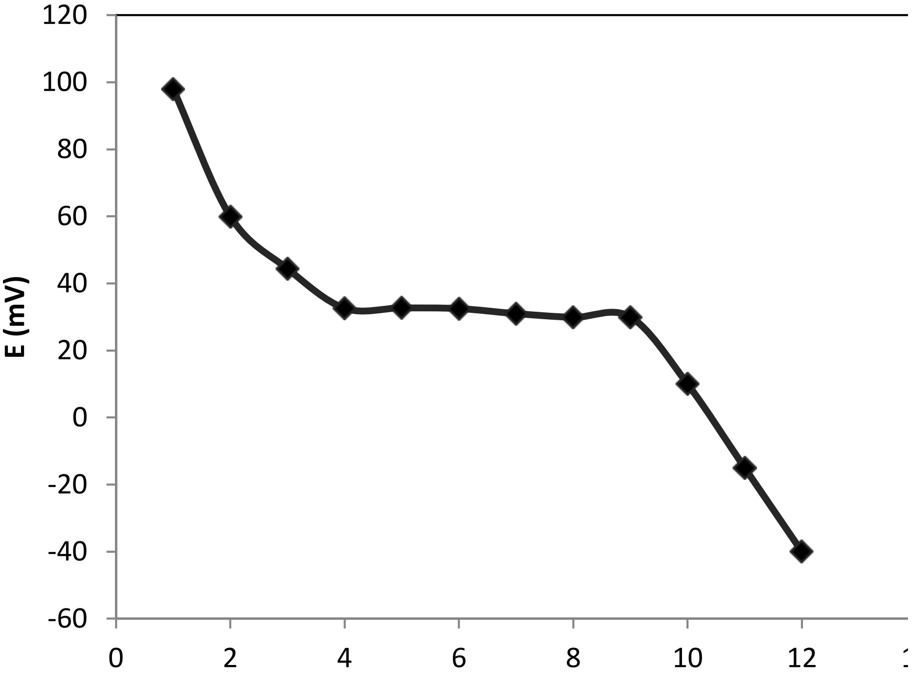

Figure 3. Effect of pH on the potential response of La(III) nano-composite CPE based on Electrode no. 11 in the test solution of La(III) ion (10^{-4} M)

3.4. Response time

Response time of an electrochemical sensor is obtained through measuring the average time required to achieve potential values within ±0.1 mV of the steady-state potential of the electrode after its immersion in a series of solutions of the target ions, each having a ten-fold difference in concentration.

A numbers of experimental parameters such as stirring, the concentration and composition of each test solution, any previous application or preconditioning of the electrode, and the testing temperature can all affect the experimental response time of a sensor [56-63]. The response time of the proposed nano-composite CPE was less than 20 s for whole concentrations.

3.5. Selectivity of the sensor

Selectivity coefficients is the most important characteristic of any sensor, specially in the case of concentration determination of the target ion in the presence of a number of other ions with higher concentration than target ion. In this work matched potential method (MPM) was used for evaluation of selectivity coefficients [64-67] of the nano-composiote based sensor and the results are given in Table 2.

As it can be seen, the selectivity coefficients of the proposed sensor are lower than 2.1×10^{-3} for all alkai, alkaline earth, heavy metal and transition ions tested. These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

Table 2. The selectivity coefficients of various interfering cations for electrode no. 11; concentration of the reference solution of La(III) ion was 1.0×10^{-5} M and the concentration of interfering ions was between 1×10^{-4} to 1.0×10^{-1} M

Cation	Selectivity Coefficient	Cation	Selectivity Coefficient
Ca^{2+}	1.9×10^{-4}	Gd^{3+}	3.3×10^{-3}
Mg^{2+}	1.5×10^{-4}	Pb^{2+}	1.7×10^{-3}
K^{+}	1.2×10^{-4}	Tb^{3+}	1.7×10^{-3}
Na^{+}	1.3×10^{-4}	Cr^{3+}	9.3×10^{-4}
Li^{+}	1.1×10^{-4}	Sm^{3+}	4.6×10^{-3}
Cu^{2+}	9.5×10^{-4}	Eu^{3+}	2.3×10^{-3}
Ho^{3+}	1.4×10^{-3}	Pr^{3+}	4.0×10^{-3}
Co^{2+}	5.1×10^{-3}	Lu^{3+}	2.4×10^{-3}
Zn^{2+}	3.4×10^{-4}	Cd^{2+}	1.4×10^{-3}
Tm^{3+}	2.1×10^{-3}	Dy^{3+}	1.7×10^{-3}
Er^{3+}	2.3×10^{-3}	Ce^{3+}	2.3×10^{-3}
Ni^{2+}	8.0×10^{-4}	Yb^{3+}	2.7×10^{-3}
		Nd^{3+}	3.3×10^{-3}

3.6. Lifetime of the Sensor

For analytical application life time of the sensor is very important. Most ion selective sensors have lifetimes ranging from 4–10 weeks after which the slope and detection limt of the sensor will decrease and increase, respectively [31-34,44,61].

Table 3. Lifetime of La(III) nano-composite CPE

Week	Slope (mV $decade^{-1}$)	Detection Limit (M)
1	19.8 ± 0.2	8.0×10^{-7}
2	19.8 ± 0.3	8.3×10^{-7}
3	19.7 ± 0.4	8.5×10^{-7}
4	19.6 ± 0.1	9.0×10^{-7}
5	19.6 ± 0.3	8.8×10^{-7}
6	19.6 ± 0.2	8.9×10^{-7}
7	19.6 ± 0.3	9.1×10^{-7}
8	19.7 ±0.2	9.2×10^{-7}
9	19.6 ± 0.4	9.0×10^{-7}
10	19.5 ± 0.2	9.3×10^{-7}
11	19.5 ± 0.3	9.5×10^{-7}
12	19.3 ± 0.3	1.1×10^{-6}
13	17.5 ± 0.3	4.0×10^{-6}
14	15.1 ± 0.3	6.5×10^{-6}

The lifetime of the proposed nano-composite base La(III) sensor was considered for a period of 20 weeks, during which the sensor was used for one hour per day and the results are given in Table 3. As it is seen, the proposed nano-composite La(III) sensor can be used for at least 12 weeks. During this time, the slope and detection limit of the sensor shows small changes. After this time, a gradual decrease in the slope from 19.8±0.2 to 15.1±0.3 mV decade^{-1} amnd a gradual increase in detection limit from 8.0×10^{-7} to 6.5×10^{-6} was observed. This phenomenon is most probaly due to the loss of RTIL and ANA from the composition of the fabricated sensor.

4. CONCLUSION

8-amino-N- (2-hydroxybenzylidene) naphthyl amine (ANA) was usd as a selective ion carrier in construction of La(III) nanocomposite carbon paste electrode. The electrodes were made based on multi-walled carbon nanotube (MWCNT), graphite, and room temperature ionic liquid (RTIL) as a suitable binder. The best results were obtained in nano-composite sensor with composition of 5% MWCNT, 10% ANA, 15% RTIL, and 70% graphite powder. The proposed sensor shows a Nernstian response (19.8±0.2 mV decade^{-1}) in a linear range of 1.0×10^{-6}-1.0×10^{-2} M with detection limit of 8.0×10^{-7} M. The response of the sensor is independent of pH in the range of 4.0-9.0. The nano-composite based La(III) sensor displayed good selectivity, response time (about 20 s), and lifetime (12 weeks).

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